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THE CRYSTAL STRUCTURE OF THE RARE EARTH RING SILICATE KAINOSITE, $Ca_2(Y,TR)_2[Si_4O_{12}]CO_3 \cdot H_2O$

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The orthorhombic unit cell of kainosite has constants of $a = 12.93$, $b = 14.30$, $c = 6.73$ A and contains four formula units of $Ca_2Y_2[Si_4O_{12}]CO_3 \cdot H_2O$. The space group is $D^{16}_{2h} = Pmnb$. The structure was determined by the heavy-atom method from weighted Fourier projections and refined using normal and difference Fourier phase projections. Kainosite is a ring metasilicate and contains $[Si_4O_{12}]^{-8}$ four-membered ring anions. The Ca and Y atoms lie within eight-cornered oxygen polyhedra of the same type (Δ-dodecahedra), but the Ca polyhedra are larger than the Y polyhedra and more distorted. The two sorts of polyhedra have shared edges and corners, and through these and also through CO_3 triangles they are connected together into a three-dimensional framework containing channels in which the four-membered $[Si_4O_{12}]$ rings lie.

About three percent of all the minerals known at present contain rare earths. The present investigation has been devoted to kainosite, $Ca_2(Y,Tr)_2 \cdot [Si_4O_{12}]CO_3 \cdot H_2O$, a representative of the most common class of rare-earth silicates (TR represents a rare earth). Kainosite was first discovered in 1886 by Nordenskjöld in the Hitterö region of Norway, and derived its name from its unusual external form (kainos means new or exceptional in Greek). A synonym for the mineral is cenosite (the Latinized form of the name). Somewhat later kainosite was found in Sweden (at the Ko mines, Nordmark) and in Canada (Ontario) [1]. In 1961, V. V. Lyakhovich and V. I. Noneshnikova discovered kainosite within the USSR, in the granitoids of Tuva. The pinkish-yellow, short prismatic crystals of kainosite have the usual association with calcite, apatite, biotite, and magnetite [2].

An analysis of the structure of kainosite must throw light upon the nature and architecture of the oxygen-silicon radical, and also upon the way in which the large Ca and Y(TR) atoms are distributed in the structure. Obeying as they do the Mendeleev-Fersman diagonal rule, and the close ionic radius relationship corresponding to this, the rare earths usually substitute for the ions Ca, Sr, and (for the heaviest rare earths) Zr in crystals, either completely, or only partially, when they occupy a single crystallographically independent position with the substituted ions. Thus in gadolinite, $Fe^{\cdot\cdot}Y_2Be_2O_2Si_2O_8$ [3], the Y atoms lie within eight-cornered polyhedra of the same type as those enclosing Ca in datolite, $Ca_2B_2Si_2O_8(OH)_2$. In aeschynite [4] also, the TR and Ca atoms occupy the same crystallographic position in a strongly deformed eight-cornered oxygen polyhedron. Other possible arrangements are observed in the structures of allanite, $CaCe(Fe^{\cdot\cdot}, Fe^{\cdot\cdot\cdot})Al_2O(OH,O)[Si_2O_7][SiO_4]$ [5], and of (TR, Sr) apatite, $(Ca, TR, Sr)[PO_4]_3(F, OH)$ [6], where the TR atoms replace Ca in only one of two independent positions.

The first x-ray investigation of kainosite established that it had an orthorhombic unit cell with $a = 12.93$, $b = 14.30$, $c = 6.73$ A and a space group of $D^{16}_{2h} = Pmnb$ for $Z = 4$ formula units per unit cell [7]. In 1963 the present authors published a preliminary communication on the structure of kainosite [8]. We had at our disposal several crystals from the Canadian deposit, received from Prof. K. Frondel. Almost all these specimens showed some degree of metamict character, but even so it was found possible to pick out two irregular-shaped specimens measuring $\sim 0.3 \times 0.4 \times 0.6$ mm which gave satisfactory x-ray photographs. A Weissenberg camera was used to obtain photographs of the equatorial and first layer lines for rotation about c, and of the zero, first, and second layer lines for rotation about *a*; during the structure refinement it was found necessary to use a photograph of the third layer line for rotation about c as well. Kainosite contains a considerable proportion of yttrium, and the edge of the Y absorption band of the K series (0.726 A) is very close to the MoKα wavelength (0.711 A); therefore, to obviate anomalous absorption in the crystals the whole experiment was carried out using AgKα and CuKα radiations. The kainosite crystals were not isometric (it was not possible to turn them into spheres because they broke easily), and absorption led to a considerable scatter in the intensity measurements, which was counteracted by averaging the data for the four independent hkL quadrants (Hk*l*). The intensities were estimated visually, by comparison with a blackening scale which altered in steps of $2^{1/4}$, from multiple-exposure films. Several reflections which fell under the goniometer clip in the AgKα radiation exposures were recorded on the photographs made with CuKα radiation. After excluding the kinematic and polarization factors from the intensities, the set of nonzero structure factors consisted of $139F^2_{hk0}$, $251F^2_{hk1}$, $303F^2_{hk3}$, $168F^2_{0kl}$, $128F^2_{1kl}$, $130F^2_{2kl}$. The strong background on the x-ray photographs, due to the partial metamict character, considerably lowered the number of nonzero reflections.

The rotation photographs about the *a* axis showed a clear periodicity in the layer line intensities; the equatorial line was strong, the first layer line very weak, the second rather stronger, the third equal in intensity to the zero layer line, the fourth weak, the fifth almost equal to the third. Thereafter the pattern was repeated; 6th, weak; 7th, rather stronger; 8th, strong; 9th, weak; 10th, strong; and so on. An analysis of the structure factor formulas for the group D^{16}_{2h} = Pmnb [9] showed that this feature could be attributed to an effect of the Y atom if its x coordinate was close to 0.05-0.06. Such an x_Y-coordinate value indicates that the Y atoms lie on a single (general) eightfold regular point system.

The heavy Y atoms were located from an analysis of the Patterson projections P(v, w) and P(u, v). The former gave unambiguous values for the (yz) coordinates, and the latter the x coordinates of Y; y-coordinates determined from the function P(u, v), had two possible values because of the halving of the b constant in this projection (the coordinates y and $\frac{1}{4}$-y were indistinguishable). The x_Y-coordinate value derived from P(u, v) agreed with that obtained earlier from the general characteristics of the x-ray rotation photographs.

The structural motif existing in kainosite was worked out from normal and weighted electron-density projections, using the heavy-atom approach. The first syntheses constructed were $\sigma(x, y)$, $\sigma(y, z)$, $C_1(x, y)$, and $S_1(x, y)$, from those experimental F_{hkl} for which the signs could be taken as the same as the signs of the contributions of the Y(TR) atoms. The number of peaks on the electron density maps was much higher than the number of atoms in the structure. To pick out the true peaks from the complete set and reject the false ones we compared the highest peaks with the identical coordinate values on all four of the projections mentioned. If the results for a given peak were contradictory on the different syntheses (or their positioning contravened standard crystallochemical distance rules), then that peak was rejected. This approach resulted in the coordinates for Ca, Si_I, and Si_{II} being found, these atoms turning out to be occupying general 8-fold positions, and it also gave the coordinates of the oxygen atoms making up the Si_I and Si_{II} tetrahedra.

Since we did not have an accurate value of the ratio Y:ΣTR at our disposal, we had to use literature results [1] on the chemical composition of kainosite. Assuming a ratio of Y:ΣTR = 3 : 1 for our specimens, we constructed an effective atomic scattering factor curve [at $\sin\vartheta/\lambda = 0$, f_{eff} = 46.2 el). In the next stage of the investigation, F_{hk0}, F_{hk1}, and F_{0kl} were recalculated using the coordinates of all the atoms already fixed, and a second series of normal and weighted electron density projections gave all the atoms in the structure and thus revealed the structural motif. The oxygen atoms were "differentiated" into O and H_2O on the basis of the balance of valences [8].

The coordinates of the atoms were refined from normal and difference Fourier syntheses, the latter excluding the contributions of the cations Y(TR), Ca, Si_I, and Si_{II}. The normal and difference syntheses were assumed to be equally valid, and results obtained from them were averaged out. (The accuracy of the difference syntheses was not high because of the large number of zero-value F_{exp} resulting from the dense backgrounds on the Weissenberg photographs.) The xy projection resolved the majority of the atoms; their coordinates were fixed from the $\sigma(x, y)$ syntheses and the phase projections $C_L(x, y, Z_j)$, where L = 1, 3. For overlapping atoms the required phase projections $S_1(x, y, Z_j)$ and $S_3(x, y, Z_j)$ were calculated [10]. Also, to eliminate the effect of the heavy Y atom on O_2 and O_3, of Ca on O_5, and of Si_{II} on O_6, the difference syntheses $\Delta\sigma(x, y)$, $\Delta C_L(x, y)$, and $\Delta S_L(x, y)$ (L = 1, 3) were constructed, and these were then combined into the phase projections $\Delta C_L(x, y, Z_j)$ and $\Delta S_L(x, y, Z_j)$ used in determination of the (x, y) coordinates of all the O and C atoms. It is worth noting that the syntheses $C_3(x, y)$ and $S_3(x, y)$ were highly effective in locating the oxygen and carbon atoms lying on the m mirror plane. These atoms overlapped one another on the xy projection (C with O_4, O_4 with O_9), and here in both pairs the difference $(z_1 - z_2)/c$, equal to 0.55, was too close to $1/2$ for them to be separated using the phase projections $S_1(x, y, Z_j)$. On the other hand, for $C_3(x, y)$ and $S_3(x, y)$ more favorable separation conditions applied, since the value $l(z_1 - z_2)/c$ was closer to $(2n + 1)/4$ [10].

From the peak height relationships on the conjugate projections $C_3(x, y)$ and $S_3(x, y)$ the z coordinates of the atoms were found, including O_9, which could not be located on the yz projection because of interference by the heavy Y. More accurate z coordinates were established from the syntheses $\sigma(y, z)$, $S_1(y, z)$, and $C_2(y, z)$,[1] from which it was easy to distinguish the Y(TR), Ca, Si_I, Si_{II} cations which were paired on the projection, and some of the O atoms. Locating the single atoms lying on mirror planes was, however, made difficult because they projected on the yz plane with halved weights, and moreover they overlapped with heavier atoms (O_4 with Si_I, O_7 with Si_{II}, O_9 with Y). To refine their z coordinates the difference syntheses $\Delta\sigma(y, z)$, $\Delta S_1(y, z)$, and $\Delta C_2(y, z)$ were constructed in addition. The atomic coordinates thus found, from a combination of normal and difference syntheses, were averaged and are given in Table 1 together with their mean errors.

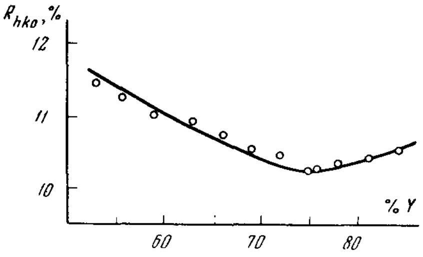
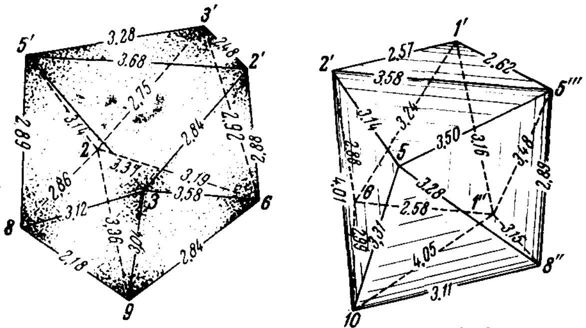


Fig. 1. Graph of R_{hk0} against percentage Y content in the total rare-earth plus yttrium present in kainosite.



Y polyhedron Ca polyhedron

Fig. 2. Projections of Y and Ca polyhedra on the xy plane. Lengths of O–O edges are given in A (based on the penultimate coordinates).

During our analysis of the kainosite structure we used the chemical analysis [1], in which the rare earths were not differentiated. R. L. Bardinskii, working in the x-ray spectroscopy laboratory of IMGRE (Institute of Mineralogy, Geochemistry and Crystallography of the Rare Earths), found the La and lanthanide contents given in Table 2 for the mineral. The analysis confirmed the high yttrium content of the yttrium-rare earth total in kainosite. However, the x-ray spectroscopy only resulted in a very approximate value for the proportion of Y in the total Y + TR, and so we refined the value of this ratio using values of the reliability factor R_{hk0} which were calculated from the (x, y) coordinates in Table 1 for a series of $f_{(Y, TR)}$ atomic scattering curves. By varying the value of $f_{(Y, TR)} = f_Y n_Y + f_{\Sigma TR} n_{\Sigma TR}$ (where n_Y was the proportion of Y in the total) from $n_Y = 53\%$ (corresponding to $n_{\Sigma TR} = 47\%$) to $n_Y = 84\%$ ($n_{\Sigma TR} = 16\%$) in steps of $n_Y = 3\%$, we obtained a minimum value of $R_{hk0} = 10.3\%$ at $n_Y = 75\%$ (Fig. 1). Thus for the kainosite the ratio of $Y:\Sigma TR = 3 : 1$ turned out to be correct. In a final recalculation of the structure factors we used the effective atomic factor $f_{Y,TR} = 0.75 f_Y + 0.25 f_{\Sigma TR}$; its value at the point $\sin\vartheta/\lambda = 0$ was 45.8 el.

The structure factors F_{hk0} and F_{0kl} calculated from the averaged coordinates, and their experimental values, are listed in Tables 3 and 4. The final reliability factors for all the nonzero reflections were as follows:

$$R_{hk0} = 9.1\% \quad (\sin\vartheta/\lambda \leqslant 0.9_0\ \text{A}^{-1},\quad B_{hk0} = 0.7\ \text{A}^2),$$
$$R_{hk1} = 9.0\% \quad (\sin\vartheta/\lambda \leqslant 1.0_5\ \text{A}^{-1},\quad B_{hk1} = 0.7\ \text{A}^2),$$
$$R_{hk3} = 12.6\% \quad (\sin\vartheta/\lambda \leqslant 1.0_5\ \text{A}^{-1},\quad B_{hk3} = 0.5\ \text{A}^2),$$
$$R_{0kl} = 12.0\% \quad (\sin\vartheta/\lambda \leqslant 0.8_5\ \text{A}^{-1},\quad B_{0kl} = 0.7\ \text{A}^2),$$
$$R_{1kl} = 14.1\% \quad (\sin\vartheta/\lambda \leqslant 0.8_5\ \text{A}^{-1},\quad B_{1kl} = 0.7\ \text{A}^2),$$
$$R_{2kl} = 13.1\% \quad (\sin\vartheta/\lambda \leqslant 0.8_5\ \text{A}^{-1},\quad B_{2kl} = 0.7\ \text{A}^2).$$

Kainosite turns out to be a metasilicate, with isolated four-membered $[Si_4O_{12}]^{-8}$ rings. A similar ring is found in the barium-titanium silicate baotite [11]. Thus kainosite is the second mineral which, on structure analysis, has been shown to contain isolated four-membered oxygen-silicon rings, although a similar phosphate ring, $[P_4O_{12}]$, was detected in 1937 by Pauling [12] in aluminum meta-

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[1] The mirror plane perpendicular to the a axis reduces $C_1(y, z)$ and $S_2(y, z)$ to zero.

TABLE 1. Coordinates and Mean Errors of the Principal Atoms in the Kainosite Structure

Atom and number present in cell	x/a	y/b	z/c
Y (TR) (8)	0.057±0.001	0.219±0.001	0.112±0.001
Ca (8)	0.079±0.001	0.453±0.001	0.300±0.003
Si_{I} (8)	0.129±0.001	0.146±0.001	0.614±0.003
Si_{II} (8)	0.129±0.001	0.431±0.001	0.835±0.002
C (8)	0.25	0.127±0.002	0.108±0.006
O_1 (8)	0.111±0.002	0.035±0.003	0.556±0.004
O_2 (8)	0.054±0.002	0.169±0.002	0.793±0.003
O_3 (8)	0.096±0.003	0.217±0.002	0.448±0.004
O_4 (4)	0.25	0.161±0.003	0.66_7 ±0.01
O_5 (8)	0.056±0.002	0.420±0.002	0.66_3
O_6 (8)	0.112±0.002	0.360±0.002	0.013±0.003
O_7 (4)	0.25	0.425±0.003	0.750±0.007
O_8 (8)	0.165±0.003	0.082±0.002	0.11_0
O_9 (4)	0.25	0.212±0.002	0.10
O_{10}* (4)	0.25	0.379±0.003	0.361±0.007

TABLE 2. Percentage Make-Up of the Rare-Earth Elements (excluding Y) in Kainosite

Rare-earth element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
% of ΣTR	0	0.4	0	0.4	15	3.9	26	2.6	19	4.3	13	2	11	2

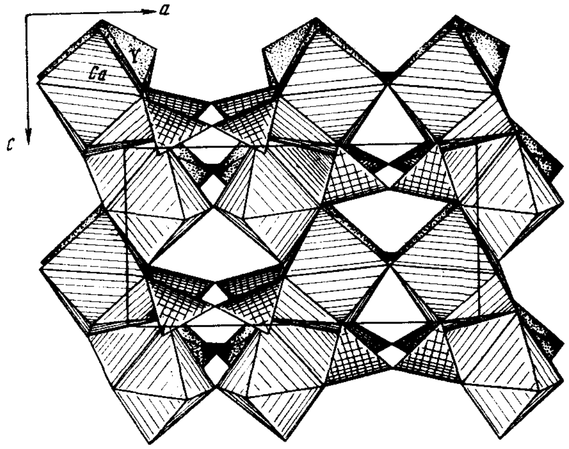

Fig. 3. Projection of half the kainosite cell on the xz plane. A network of Ca polyhedra passes through the middle of the cell parallel to (010), with attached four-membered $[Si_4O_{12}]$ rings and a lower layer of Y polyhedra, joined in pairs through CO_3 triangles.

phosphate, $AlPO_3$. In kainosite the Ca and Y atoms each separately occupy a crystallographically independent eightfold regular point system. Both cations lie within similar eight-cornered oxygen polyhedra with 12 triangular faces, i.e., Δ-dodecahedra (Fig. 2), although the Ca polyhedra are larger than the Y polyhedra and more distorted. Polyhedra of this type are typical of many Ca compounds (anhydrite, $CaSO_4$ [13]; Ca garnet [14]; scheelite, $CaWO_4$ [15]; hydroboracite, $CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$ [16]; and others), and also of Zr and Y compounds (zircon, $ZrSiO_4$; xenotime, YPO_4).

Figures 3 and 4 show details of the kainosite structure in projection on the xz and yz planes. Along the [010] direction alternating Ca and Y polyhedra, linked together through shared edges, are

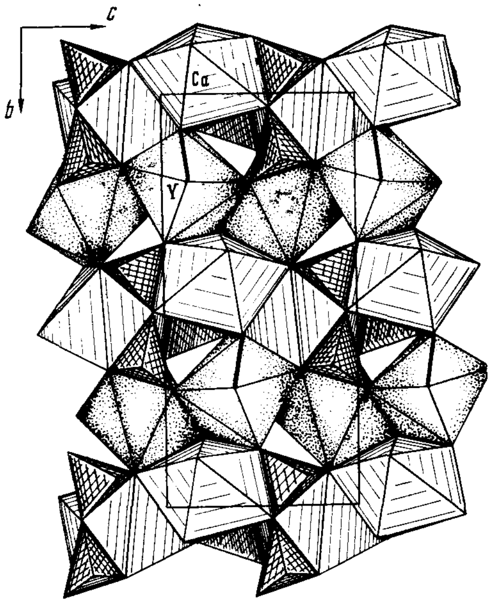

Fig. 4. Projection of half the kainosite cell on the yz plane ($-1/4 \leq x \leq 1/4$). The corrugated walls of Y and Ca polyhedra parallel to (100) can be distinguished, with connecting CO_3 triangles (heavy lines) and halves of four-membered $[Si_4O_{12}]$ rings.

TABLE 3. Experimental and Calculated Values of the F_{hk0} Structure Factors in Kainosite. A Correction is Included in F_{calc} for a Temperature Factor of $\exp[-0.7\ A^2 \cdot (\sin\vartheta/\lambda)^2]$. R_{hk0} = 9.1% for $F_{exp} \neq 0$ ($\sin\vartheta/\lambda \leq 0.92\ A^{-1}$)

h \ k	0	2	4	6	8	10	12	14	16	18	20	22	24	26
0	1284 —	−165 128	80 77	−171 185	−139 177	−89 80	−155 181	242 260	−169 168	110 88	−75 60			
1	0	−66 50	272 275	−68 70	64 61	−114 114	35 <26	−85 84	−15 <31	60 56	−22 <32			
2	293 204	−178 172	230 241	−66 63	−55 43	12 <24	−114 121	80 82	−116 114	102 102	−37 <33	56 59		
3	0	−38 41	361 373	−138 129	215 229	−213 237	72 65	−119 120	−15 <32	40 50	−72 64	82 83	−52 59	82 92
4	−196 210	−140 152	40 40	4 <20	50 <23	131 121	5 <27	−50 42	−5 <32	40 42	−37 <35	−10 <36		
5	0	−36 30	329 340	−221 227	237 259	−149 132	109 117	−65 61	10 <33	−7 <35	−107 125	91 79	−71 62	78 67
6	−394 370	104 103	−126 123	39 <22	42 <24	30 <26	151 148	−52 43	84 83	−98 105	20 <36	−47 <38		
7	0	−94 92	6 <22	−104 96	129 125	−34 <27	76 71	−10 <30	8 <33	17 <35	−39 <37	39 <39		
8	−112 116	175 203	−234 233	102 93	43 45	−102 93	103 106	−31 <32	123 118	−127 136	53 <38	−68 69		
9	0	−44 41	10 <25	7 <25	−128 133	−31 36	12 <32	22 <34	35 41	65 68	35 <39	−30 <41		
10	−256 200	171 156	−52 57	80 85	21 <28	−65 52	22 <33	−129 132	86 94	−78 80	87 72	−4 <42		
11	0	43 38	−145 156	67 60	−155 156	59 62	68 65	61 49	34 <37	16 <39	65 48	−63 43		
12	−68 50	83 84	8 <28	−8 <29	−17 <31	1 <32	−23 <33	−90 87						
13	0	57 62	−168 185	75 81	−60 68	147 152	−80 81	42 41					98 60	
14	42 31	−1 <26	46 54	−28 <32	−37 39	−22 <34	−26 <36	15 <38						
15	0	62 65	78 76	137 148	−26 <34	106 106	−62 64	10 <39	−57 51	−71 51			92 63	
16	195 236	−88 84	21 <34	−32 <34	−10 <35	−4 <37	−36 <38	104 104	−59 72					
17	0	31 <35	73 70	98 101	−38 <37	−7 <38	−15 <39	−18 <41	−31 <42					
18	75 70	−115 124	67 81	−34 <37	15 <38	64 73	21 <40	68 <42	83 97					
19	0	−14 <37												
20		−96 92												
21				−130 134	63 82									
22														
23				−85 87		−65 63								
24		62 53												

laid out in columns, with the Ca−Y−Ca axis deviating slightly from a straight line. Two adjacent mirror-equivalent columns are joined together into a double ribbon through shared corners and CO_3 "glueing" groups. In the xz projection the ends of these ribbons form a chess-board pattern, alternating with channels in which the isolated $[Si_4O_{12}]$ island rings lie. Polyhedra of the same type are also linked with one another along the [001] axis, but here they form a zigzag chain. Along the b axis the Ca chains alternate with similar Y chains and together these form a corrugated wall parallel to the yz plane. These discrete walls divide up the whole structure. In the wide gaps between the corrugated walls, all the remaining polyhedral units of the structure are collected, i.e., the planar CO_3 groups and the discrete $[Si_4O_{12}]$ rings.

Table 5 gives interatomic distances in the kainosite structure. The Y−O distances in the eight-cornered Y polyhedron lie between 2.24 and 2.52 A,

TABLE 4. Experimental and Calculated Values of the F_{0kl} Structure Factors in Kainosite. A Correction is Included in F_{calc} for a Temperature Factor of $\exp[-0.7\ A^2 \cdot (\sin\vartheta/\lambda)^2]$. R_{0kl} = 12.0% for $F_{exp} \neq 0$ ($\sin\vartheta/\lambda \leq 0.83\ A^{-1}$)

l k	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	1284 —	0	−34 37	0	−310 279	0	−45 36	0	81 78	0	108 89	0	−61 69	0
1	0	−4 <10	−353 240	−137 141	−154 145	8 <15	246 239	−39 44	96 87	63 28	−87 82	−3 <32	−82 80	
2	−165 150	−33 38	−165 146	−99 87	208 198	65 52	119 108	49 37	−129 132	−30 <28	−62 64	18 <32	28 36	
3	0	−56 57	218 192	61 52	−102 73	112 97	−69 91	−19 <24	−69 56	−25 <28	34 <31	5 <32	52 38	
4	80 82	36 27	36 <14	137 121	−74 66	58 44	−79 70	−86 74	13 <28	−35 <29	35 <31	81 69	−40 60	
5	0	125 132	−27 <14	−126 102	−118 103	−100 102	110 94	19 <25	21 29	105 105	−30 <32	26 <32	−2 <33	−45 55
6	−171 181	−160 183	40 36	−290 239	114 95	103 89	−7 <25	157 152	−28 <29	−49 49	3 <33	−48 47	2 <34	−44 47
7	0	−265 256	92 79	143 152	−78 70	211 187	12 <25	−31 <26	−57 52	−174 155	28 <33	−20 <34	31 <35	73 65
8	−140 173	389 322	131 112	257 244	−9 <21	−63 64	−46 36	−120 117	54 59	−16 <32	−1 <34	104 80		
9	0	196 213	−4 <19	−113 100	−33 <21	−219 231	−18 <26	94 80	−26 <28	78 74				
10	−89 66	−46 47	61 58	−136 126	−68 53	5 <24	−42 <26	126 133	49 50	16 <33	−23 <35	−79 81		
11	0	−55 56	−104 108	126 120	15 <23	45 49	25 <26	16 <28	32 <29	76 68	−13 <35	−14 <37	−25 <39	43 50
12	−155 184	89 91	−49 33	93 95	63 70	−46 <26	67 62	−40 <28	−30 <30	14 <34	−63 54	5 <37	46 55	
13	0	28 <22	112 113	26 <24	82 73	−113 80	−129 75	25 <29	−70 62	37 <36	62 55	−9 <38	56 58	
14	242 266	−76 57	56 37	−33 <25	−184 220	−20 <27	−43 40	31 <30	108 95	5 <37	39 38			
15	0	−36 46	−221 263	57 54	−5 <27	−13 <28	101 100	−8 <32	88 75	−31 <38	−68 63	−12 <40	−65 65	
16	−169 215	−93 79	−57 58	45 59	118 138	18 <29	83 83	−44 <35	−63 55	26 <39	50 51			
17	0	18 <26	103 109	14 <28	43 52	21 <30	−117 137							
18	111 91	−60 46	22 <28	36 <28	−65 71									
19	0	42 51	−40 48	50 46										
20	−75 83	−67 75	−19 <30	71 74	81 67									
21	0	−65 70	71 68	7 <31	23 <32	113 108	−48 <37	−40 <39	−11 <41	−73 67				
22	62 <31	83 97	2 <32	96 79	−14 <33	−35 <35	−24 <37	−80 78						
23	0	81 83	−22 <33	97 86										
24	27 <33	−15 <34	−27 <35	97 133										
25	0	−31 <35												
26	−12 <35	70 93												

the O–O edges are from 2.75 to 3.68 A (Fig. 2); exceptions to this are the two edges O_8–O_9 = 2.16 A (shared between CO_3 triangles) and O_2–O_3 = 2.48 A (simultaneously forming the edge of a Si_I tetrahedron). In the Ca polyhedron six Ca–O distances lie within the narrow range 2.24-2.53 A, two more are 2.73 and 2.96 A long, and the remainder exceed 3.7 A. The O–O edges in the Ca polyhedron (Fig. 2) vary from 2.88 to 4.05 A, not counting three shorter O–O edges which simultaneously form sides of SiO_4 tetrahedra ($O'_1 - O'_2$ = 2.60, $O'_1 - O'''_5$ = 2.60 and $O''_1 - O_6$ = 2.55 A). The average distances in the CO_3 triangles and in the oxygen-silicon tetrahedra are in agreement with standard values and with those found in the structures of two other carbonate-silicates, tilleyite [17] and spurrite [18, 19]. The O–C–O bond angles indicate (within the limits of experimental error) that the carbon atom lies in

TABLE 5. Interatomic Distances in the Kainosite Structure, in A *

Si_I - tetrahedron		Si_{II} - tetrahedron		Y-polyhedron	
Si_I-O_3	1.57	$Si_{II}-O_5$	1.50	$Y-O_6$	2.24
Si_I-O_2	1.58	$Si_{II}-O_6$	1.58	$Y-O_2$	2.26
Si_I-O_4	1.62	$Si_{II}-O_7$	1.67	$Y-O_3$	2.32
Si_I-O_1	1.65	$Si_{II}-O_1''$	1.67	$Y-O_8$	2.40
				$Y-O'_3$	2.44
Average	1.60_5	Average	1.60_5	$Y-O_2'$	2.47
				$Y-O_5'$	2.49
O_2-O_3	2.48	$O_1''-O_6$	2.55	$Y-O_9$	2.52
O_1-O_2	2.60	O_5-O_7	2.57	Ca-polyhedron	
O_3-O_4	2.60	$O_1''-O_5$	2.60	$Ca-O_8''$	2.24
O_1-O_4	2.65	O_5-O_6	2.61	$Ca-O_6$	2.38
O_2-O_4	2.67	O_6-O_7	2.69	$Ca-O_2'$	2.45
O_1-O_3	2.71	$O_1''-O_7$	2.72	$Ca-O_{10}$	2.48
Average	2.62			$Ca-O_5$	2.51
		Average	2.62	$Ca-O_5'''$	2.53
CO_3-triangle					
$C-O_9$	1.22	O_8-O_9	2.16	$Ca-O_1''$	2.73
$C-O_8$	1.27	O_8-O_8'''	2.20	$Ca-O_1'$	2.96

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*The prime ' denotes atoms related to principal atoms through a screw axis, two primes " means relation through a b glide plane, three primes ‴ a center of symmetry, and the superscript m a mirror plane.

the plane of the oxygen triangle. Individual Si–O distances are shorter than the average value of 1.60 A for those O connected to one Si (i.e., O_2, O_3, O_5, O_6), and longer for O_1, O_4, and O_7, which are joined to two Si through bonds passing in opposite directions ($Si_I-O_I-Si_{II}'' = 137°$, $Si_{II}-O_7-Si_{II}^m = 140°$, $Si_I-O_4-Si_I^m = 150°$).

The crystal structure of kainosite is a good example of the basic considerations governing "second-chapter" silicate crystal chemistry [20]. The skeleton of the structure is made up of the polyhedra formed around the large Ca and Y cations, which are firmly bound together. The four-membered oxygen-silicon rings occupy spaces in the three-dimensional framework and play a subordinate role in determining the architectural pattern.

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